Evaluating Source Profiles Using Pair Ratio Distribution (PRD) Method: Applications to BRAVO and CRPAQS Studies

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Introduction

Source profiles measure the relative abundances of species from specific emission sources, and are the basis for various receptor models which attempt to quantify source contributions to ambient pollutant concentrations. To determine those species that are the best markers for a source contribution, the pair ratio distribution (PRD) method is developed to compares ratios of each pair of species abundances within and inter- source categories. Why compare ratios instead of absolute mass fractions in the source profiles?

1. Source variability: larger variability may exist in the emission-contributing species than tracer species.

2. Ambient contamination: some source profiles are measured in source dominated environments that may include minor contributions from other source types (e.g., roadside exhaust samples).

3. Measurement uncertainty: source profiles need to be normalized to emitted PM mass. Inaccurate mass measurements increase the uncertainties of all abundances, even those that are precisely measured (e.g., some elemental measurements are more precise than the mass measurement).
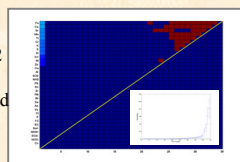
Ex. Rb/K ratio of mass-

Method Description

1. Determine uncertainties of single species in the source profiles: analytical uncertainties from sample volume, analytical noise, and blanks.

2. Determine ratios of paired species: use the species of lower uncertainty as denominator. For replicate profiles, the mean of ratios is calculated, and uncertainty of the ratio is the root mean square uncertainty or standard deviation of individual ratios, whichever is larger.

3. Compare each ratio of paired species with its uncertainty to determine species of statistical significance, and group these species to form characteristic patterns of the respective source profile.

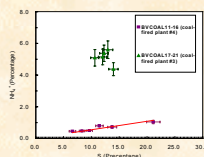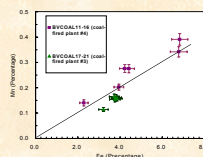## Combine different source emissions

Compare profiles from different sources to determine the common pattern for compositing the profiles.

Example:

Combine coal burning profile #1 and #2 together. The common pattern only consists of Fe, Ca, Sr, Mn, Ti, Cr, K, and S. They can be common tracers for coal burning.

Ex.: The Mn/Fe ratios in the coal burning profile #1 & #2 are similar, but NH_4^+/S ratio shows significant variations. Coal burning #2 produces much higher NH_4^+.

Differentiate similar source profiles: Identify species that differentiate source profiles

Calculate values (R) and uncertainties (U) of the differences of pair ratios from two similar source profiles/categories. Pair ratios with R/U ratio > 2 can help differentiate the two source profiles.

Ex.: Compare two resuspended fly ash samples with coal-burning profiles.

Coal-fly ash #3 – coal burning #1: differentiated: P, NO_3^-, Fe, Mn, Ca, and Ti.

BVCLFA03: Resuspended coal fly ash sample from a Texas electric utility's 600-megawatt power plant #2.

Coal-fly ash #1 – coal burning #1: differentiating species: Zn and Ni

BVCLFA02: Resuspended coal fly ash sample from a Texas aluminum processing facility's 545-megawatt power plant #4.

•The fly ash #1 was collected from the coal-burning #1 utility (Unit 4), and its profile resembles the coal-burning #1 profile in PSD, but they differ in the Zn and Ni abundances.

PM₂.₅ Source profiles from replicate measurements
[The red area indicates a coefficient of variation > 2 (95% confidence level) for the paired species (i.e., the pair ratios of replicate measurements are consistent).]

Coal-Burning #1: Rb, Fe, Ti, Ca, K, Si, Sr, Cu, Ni, Mn, Cr, and S.
BVCOAL11-16: Stack emission from plant #4 (a Texas electric utility's 545-megawatt power plant Unit 4 [supplying electricity to an aluminum processing facility] equipped with dry limestone scrubber to remove acidity,) and perflow material (to remove fluorine) and fueled by pulverized lignite coal)

Coal-Burning #2: Zn, Ti, SO_4^{2-}, Sr, Cr, V, Ca, S, Si, Al, K^+, NH_4^+, Fe, Mn, and K.
BVCOAL17-21: Stack emission from plant #3 (a Texas electric utility's 550-megawatt power plant Unit 3 equipped with an electrostatic precipitator and baghouse and fueled by lignite coal)

Wood-Burning #1: Br, Se, K^+, K, Cl, TC, Na^+, NH_4^+, and SO_4^{2-}.
BVBURN17-7-18: Open burning of cut tamarisk shrubs/trees to stimulate wildebee emissions.

Wood-Burning #2: Cu, S, Al, TC, Fe, Cl, SO_4^{2-}, K, and Br.
BVBURN5-6,16: Open burning of cut mesquite shrubs/trees to simulate wildfire emission.

Oil refinery: Zn, Ca, K, S, Se, Mn, Al, Na^+, Sr, Rb, Ni, Fe, V, Ti, and Zr.
BVCATH1-05: Stack emission from a Texas refinery's heavy oil catalytic cracking unit equipped with an electrostatic precipitator.
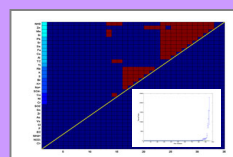
Cement kiln: NH_3, Zn, Mn, Si, Pb, Sr, Se, Fe, Ca, Al, (Rb, K^+, K, Br, S, Na^+, SO_4^{2-})
BVCEMT01-06: Stack emission from a Texas cement kiln (#1), equipped with an electrostatic precipitator and fueled by a mixture of 70% low-sulfur Wyoming coal, 10% pet coke, and 20% scrap tires).

On-road mobile: Zn, NH_3, and EC.
BVRSMV04.32-34,41-42: Roadside sample from intersection of Presto La Trinidad and Commerce, San Antonio, Texas.
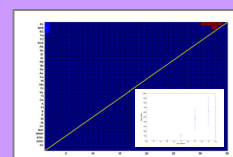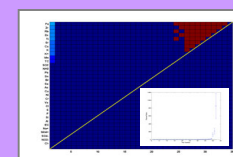
Resuspended BV soil: Fe, Zr, Rb, Zn, Ti, Sr, Ca, K, and K^+.
BVSOIL02,05,07,08: Soil sample from south Texas (PM_x)

Compare CRPAQS and BRAVO source profiles

Compare CRPAQS soil and vegetative burning source profiles acquired at central California with BRAVO profiles from Texas.
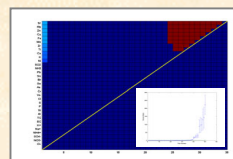
Resuspended CA soil: Sr, Rb, Zn, Cu, Fe, Mn, Zr, Ti, and Ca.
FDTOMIA-C,2A,3A: Agricultural soil from tomato fields 1,2, and 3, East-Central Fresno County, CA (PM_x)
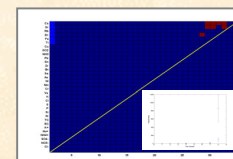
Resuspended CA soil – BV soil: Differentiating species: Ca and Sr.

•These two soil profiles are very similar, and only show significant differences in Ca and Sr abundances. The figure on the upper right illustrates Zn/Fe and Sr/Fe ratios in the two soil samples. The Zn/Fe ratios in the two soil samples are consistent but Sr/Fe ratios are not. The BRAVO soil contains much higher Sr and Ca.

CRPAQS oak burning & BV wood-burning #1: Common species: None.
CRPAQS OAK burning: California hardwood, oak, Fireplace, ventilated, open fire, with grate, dried wood, dilution tunnel, collected at DRI, Stead, Reno.

CRPAQS oak burning & BV wood-burning #2: Common species: Zn, TC, Cu, Fe, S, and SO_4^{2-}.

CRPAQS oak burning is more similar to BV wood-burning #2 (Mesquite) than #1 (Tamarisk).

•Burning hard-wood oak produces emissions more similar to burning mesquite than burning tamarisk. This is not unexpected since tamarisk is a shrub-type soft wood.

•Ratios of Zn, TC, Cu, and S could be good tracers for hard wood burning, though emission profiles acquired from open burning generally show large variability.
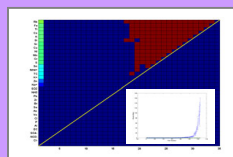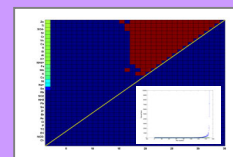
Conclusions

The paired ratio distribution (PRD) method identifies marker species in source profiles, resolving common patterns, and differentiating similar source profiles, based on comparing ratios of paired species. This method reduces biases caused by contamination from other sources and uncertainties in the particulate mass measurements. The strength of PRD relies on high quality replicate measurements from a single source or multiple measurements for sources within the same category. CRPAQS source profiles are being obtained from several source types with an expanded number of species abundances for application of the PRD method.

References
1. Chow, J. C., Watson, J. G., Kuhns, H. D., Etyemezian, V., Lowenthal, D. H., Crow, D. J., Kohl, S. D., Engelbrecht, J. P., and Green, M. C., Source profiles for industrial, mobile, and area sources in the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Chemosphere 54[2], 185-208. 2003. 2. Chow, J. C., Watson, J. G., Ashbaugh, L. L., and Magliano, K. L., Similarities and differences in PM₁₀ chemical source profiles for geological dust from the San Joaquin Valley, California. Atmospheric Env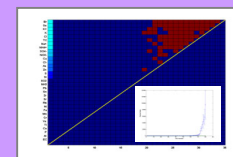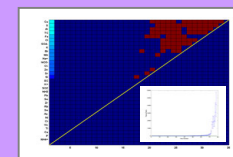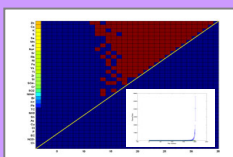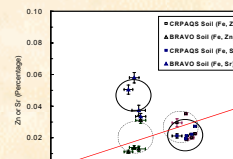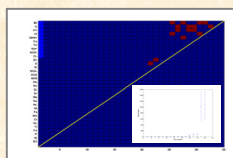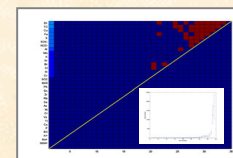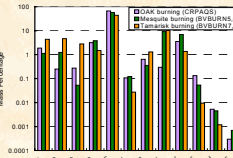ironment 37[9-10], 1317-1340. 2003